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THE ZETA POTENTIAL IN CRUDE EXTRACTS OF SOME HIBISCUS PLANTS FOR WATER TREATMENT

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Abstract
The aim of this study was to investigate the coagulation mechanism and turbidity removal potential of some members of the Hibiscus family namely; Okra crude extract (OCE), Sabdariffa crude extract (SCE) and Kenaf crude extract (KCE) in treating both river water and synthetic kaolin water samples. Experiments were conducted in a series of batch tests using standard jar test apparatus and a Zeta sizer Nano particle analyser. The results show that while the coagulation mechanism of the extract in treating synthetic kaolin water was likely due to charge neutralisation and bridging action, in the river water it was by adsorption and bridging effect caused by raw water constituents. In addition, turbidity removal performance in synthetic kaolin water sample was 94, 88 and 85% using OCE, SCE and KCE respectively. Similarly, the efficiency of OCE, SCE and KCE in treating river water was observed to be excellent, achieving 98, 96 and 83% respectively. Overall, the coagulation mechanism and residual turbidity in water treated using Hibiscus seed extracts could be a feasible alternative to the conventional chemical to provide rural people with clean water in developing countries.

Keywords: Coagulation mechanism; zeta potential; protein; crude extract; water treatment

1. Introduction

Coagulation and flocculation are considered to be the principle behind the treatment of both water and wastewater in most conventional plant. Coagulation is simply the process of destabilizing the particles by introducing metal salts to chemically change the stability of the particles in solution, such that the charge maintaining their stability is overcome by a simple charge neutralization action where the aggregate are smaller and dense (Gregory, 2005). Coagulation mechanism is measured by the rate of destabilization of the particles. The process is achieved through destabilization and precipitation mechanisms, such as surface charge modification, double layer compression, adsorption and particle bridging (Duan and Gregory, 2003, Gregory, 2009).

Flocculation on the other hand is a slow mixing process (i.e. orthokinetic aggregation) used after the particles are coagulated. Flocculation process brings together (bridging) the destabilized smaller, micro-flocs resulting from coagulation into contact with one another to form larger macro-flocs (Klimpel and Hogg, 1986). Flocculation step is crucial and is measured by the rate of collision efficiency between particles which do not settle and are thus difficult to remove by sedimentation. In water treatment, floc formation depends on the collision efficiency (α) between the particles (Gregory, 2005) where the intensity of mixing is reduced as the water proceeds through this process to achieve optimum performance.

It is noteworthy that coagulation and flocculation processes are dependent on the zeta potential of the solution, which is the potential difference between the external thin surface layer of ionized particle and that of the surrounded oppositely charged ions from the liquid.

In a simpler term, it is a measure of surface charge on particles in suspension. It indicates the behaviour of particles in a system and is widely related to the stability of the suspended

materials under given set of water characteristics. Thus, any zeta potential near zero reveals the minimal electrical repulsive force and so increases the tendency of capture (Gregory, 2005). All particles in water are invariably negatively charged (Dentel, 1991, Sharp, 2005). However, changes in general water characteristics and environment effects which generate process compliance issues, have resulted to increased application of charge measurement in the water industry. Most natural colloids in water exhibit a negative zeta potential of between – 5 and − 40 mV (Sharp, 2005). Zeta potential is a property of an electrically charged interface which is measurable and is determine from any of following methods; electrophoresis, electro-osmosis, stream potential and sedimentation (Branko, 1992, Delgado *et al.,* 2005).

On the other hand, the state of a charged surface is characterized by spatial distribution of ions around the particle whereas the zeta potential is the characteristic of the charged surface. Therefore, both zeta potential and charge are obtain from the same measurement (ionic measurement) using the same methods (Delgado *et al.*, 2005). It is noteworthy that the use of anionic compounds to flocculate negatively charged particle is debatable. However, in contradicting the theory of double layer compression when dealing with anionic coagulant, La Mer (1966) used potato starch which is an anionic compound to flocculate kaolin particles in water. Similarly, Diaz *et al.* (1999), Zhang *et al.* (2006) and Miller *et al.* (2008) flocculated kaolin water with an anionic compound extracted from C*actus latifaria* and *Cactus opuntia* and observe a turbidity removal performance of > 90%. La Mer (1966) argued that the anionic compound hydrolysed in solution where the COOH group replaces the amino groups and increases the adsorption effect of the anion at higher dosage. Under high dosage, the adsorption ability increases and outweighs the electrostatic repulsions between the coagulant and the particle which later transformed to bridging action. Thus, it is not out of place to say an anionic extract could flocculate negatively charged particles in water through adsorption and bridging action, and not by charge neutralization because of electrostatic repulsion between the coagulating compounds and the negatively charged particles.

Therefore, the aim of this study was to identify the zeta potential of the three crude Hibiscus seeds, viz, Okra, Sabdariffa and Kenaf and evaluates their mechanism of coagulation in drinking water treatment.

2. Materials and methods

All the three Hibiscus seed (okra, sabdariffa and kenaf) samples were obtained from Marama in Hawul Local Government area of Borno state-Nigeria. The seeds were harvested from mature plants and the seed kernels were manually removed from the seedpod/capsules, followed by washing with tap water in Civil Engineering laboratory (at the University of Birmingham, UK) to eliminate any surface contamination. The seed was ground into a fine powder for 2 minutes using a Tema laboratory disc mill. The ground seed powders were then sieved in a set of sieves arranged in descending order. The powders retained in the 212 µm and 300 µm sieve sizes were combined, and thoroughly mixed and used in the preparation of the suspension.

2.1 Preparation and extraction of the coagulants

The crude seed extract (CSEs) were prepared from the ground seed powders following (Jones and Bridgeman, 2016a) where 1.0 M NaCl solutions were added to the seed powder to make 2% (w/v) suspension. The suspension was vigorously stirred using a magnetic stirrer for 15 minutes at room temperature (19±2°C). The suspension was then centrifuged at 4000 rpm for 10minutes using a Heraeus Megafuge16 (Thermo Scientific, Germany). The suspension was decanted and the residual solids were dried in an oven at 50°C overnight. The weight of the dried solid material was measured to ascertain the amount of seed powder used in making the suspension. The decanted suspension was then filtered through Whatman No. 42 and was then used as coagulant in a series of jar test experiments.

2.2 Lipid extraction

The combined seed powders were defatted using high-grade hexane in a Soxhlet extractor. 20 grams of the ground powder was extracted in the extraction thimble of the apparatus. For efficient extraction, two litres of solvent volume (high-grade hexane) was heated to 60 °C. The process was run continually for 8 hours with each complete cycle taking between 2 to 3 minutes. The residue from the extraction thimble was dried overnight at room temperature (19±2°C), the dried residue was then ground into a fine powder using pestle and mortar. The ground oil-free powder was then employed in the subsequent protein purification process.

2.3 Protein purification

Protein purification was conducted according to Jones and Bridgeman, (2016b) and Jones (2017) where a 1 ml HiTrap Q HP anionic ion exchange column, (GE Healthcare, Sweden) was used for the purification of the proteins of interest.

2.4 Collection of water sample

River water samples were collected in Bourn Brook river adjacent University of Birmingham train station in a set of one-litre (1 L) sterilised Plastic containers. A total of sixty (60) representative samples (twelve sets each i.e. 12 L) from 5 location across the river were collected for the experiments. The collected water (60 L) was emptied in a single sterilised plastic bucket and the low-turbid water allowed to settle naturally before conducting any test. Water samples were kept in a refrigerator at 4 °C and the tests conducted within 4 hours of collection to avoid sample deterioration.

2.5 Jar test experiments

Jar tests were carried out using a conventional apparatus (Phipps and Bird, 7790-900B, USA) in triplicate, comprising six 1L beakers following (Jones and Bridgeman, 2016a) to evaluate the optimum coagulant dose for the determination of zeta potential in water.

Zeta potential was measured using Zetasizer Nano ZSP (Malvern instrument, UK). Instrument temperature was kept constant at 25°C throughout the test runs. An average of 10 measurements was made for each sample and the measured data automatically logged onto a computer and the zeta potential measurement recorded. A mean value of 7 measurements was calculated using the Zetasizer software.

The zeta potential measurement was undertaken on the raw water sample and on the treated water samples after 1hr sedimentation in a series of jar test experiments to determine the coagulation mechanism and performance of the samples. Measurements were conducted with ±2% accuracy over the entire measurement cycle.

3. Results

3.1 Coagulation mechanism of the extracts in synthetic kaolin water

The results on the surface charge potential and turbidity reduction by OCE, SCE and KCE on a synthetic water with a turbidity of 55 NTU are presented in Figure 1. The results show that the kaolin water has an initial zeta potential of −15.5 mV, indicating that kaolin particles are negatively charged (Katayon *et al.*, 2004, Miller *et al.*, 2008). During the coagulation process, a 20 mg/l dose of OCE was used to achieve a residual turbidity of less than 3.5 NTU, corresponding to 94% removal efficiency while the zeta potential of OCE (O_{zp}) treated water increased from −15.5 to −4.39 mV likely due to adsorption. The significant increase in zeta potential of the water after treatment could be due to the effect of some tap water constituents. In addition, the surface charge potential of OCE was −8.3 mV as shown in Table 1. Incidentally, the zeta potential of OCE also increased substantially from −8.3 to −4.39 mV in the clarified water. Earlier work by Ndabigengesere *et al.* (1995) reported the zeta potential of *Moringa oleifera* (MO) stock solution to be +6 mV and suggested that MO consists of cationic proteins. The amount of protein used for coagulation was 2.036 mg from the 20 mg/l dose, indicating that 17.964 mg of the extract are contaminants compounds in the seed that may affect its coagulation ability. Further coagulant dose addition was also investigated in order to understand the effect of increasing the anionic charge in the treatment process. The addition of more dose from 40 to 100 mg/l resulted in increased turbidity due to re-stabilisation and at the same time, the zeta potential decreased further from −4.39 mV at an optimum dose to −6.6 mV at 40 mg/l, followed by a linear reduction to −8.06 mV at 100 mg/l dose.

The coagulation mechanism of SCE in treating synthetic water was investigated. Optimum performance was achieved with 60 mg/l dose which yielded a reduction of 88% from 55 NTU to less than 7 NTU. At the optimum dose, the zeta potential of SCE (S_{zp}) treated water increased from −15.5 to −6.31 mV. Table 5.4 also shows the surface charge potential of SCE as a coagulant to be −6.4 mV, higher than that of OCE, which was −8.3 mV. Coagulant dose above 60 mg/l resulted in an increase in residual turbidity. For example, at a 100 mg/l dose, the residual turbidity was 10.82 NTU, representing 80% reduction and the zeta potential also decrease from −6.31 mV with 60 mg/l dose to −9.44 mV at 100 mg/l due to charge reversal. The coagulation mechanism presented by SCE was typical of charge neutralisation. The amount of protein used for coagulation was 5.058 mg while the remaining 54.492 mg used in the 60 mg/l dose extract are contaminants.

The application of KCE as a coagulant was also evaluated and its coagulation mechanism determined after treating 55 NTU water. The surface charge potential of KCE was found to be −8.3 mV similar to that of OCE (Table 1). Various doses of KCE sample was added to the synthetic water and the residual turbidity decreases continually until the maximum dose of 100 mg/l. Turbidity removal performance was 85%, with 100 mg/l as the optimum dose.

However, the work presented here observed that KCE behaved differently to OCE or SCE, and the zeta potential response was quite the opposite of coagulation mechanism of OK and SB seeds. In KCE, residual turbidity decreased continually as coagulant dose increased which resulted in an increase in zeta potential until the maximum dose of 100 mg/l was reached. The zeta potential of KCE (K_{zp}) final water increased from −15.5 to −6.67 mV at the end of the treatment.

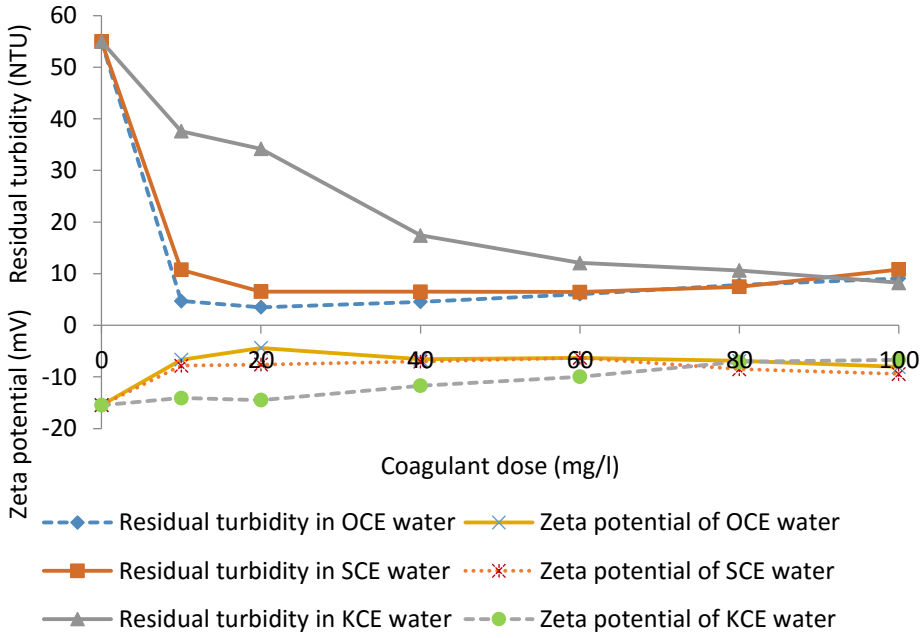

Figure 1: Coagulation mechanism of OCE, SCE and KCE in 55 NTU synthetic water.

The degree of charge neutralisation action was different requiring more dose to destabilise the kaolin particles. The amount of protein used for coagulation in the KCE treated water was 6.31 mg from the 100 mg/l dose whereas the remaining 93.69 mg in the extract was contaminants added into the treatment process.

Table 1: Surface charge potential of crude, purified and contaminants in Hibiscus seeds.

Samples	OK	SB	KE
Zeta potential of Purified seeds	−10.1	−11.4	−8.1
Zeta potential of Crude seed extracts	−8.3	−6.4	−8.3
Zeta potential of Contaminants	−10.3	−14.1	−5.1

While OCE and SCE required doses of 20 and 60 mg/l respectively, the KCE sample used the maximum dose of 100 mg/l to destabilise the kaolin particles in the raw water to achieve turbidity reduction.

3.2 Coagulation mechanism of the extracts in river water

To understand further the coagulation mechanisms of the extracts in water treatment. OCE, SCE and KCE were applied to treat river water with similar range of doses used in treating the synthetic water. Figure 2 shows the performance of varying doses of OCE, SCE and KCE in river water with a turbidity of 19 NTU and zeta potential of −12.3 mV.

The results show a maximum turbidity removal of 98% was achieved with 40 mg/l dose of OCE, and the zeta potential remained largely unaffected at −12.6 mV. The addition of more coagulant dose eventually led to overdosing leading to re-stabilisation. The zeta potential in the water marginally increased from −12.3 to −11.7 mV, with 100 mg/l dose. Overall, there was a relative change in zeta potential and the optimum dose did not correspond to the highest zeta potential value in the water due to background effect (zeta potential) from NOM in river water. Under this condition, the coagulation mechanism was by adsorption and bridging action.

Meanwhile, when a 40 mg/l dose of either SCE or KCE was used, turbidity reductions were 96 and 83%, from 19 NTU to less than 0.68 and 3.25 NTU respectively. At the optimum coagulant dose, the zeta potentials value increased marginally in SCE to −11.4 mV while −10.6 mV was found in KCE treated water. Again, the coagulation mechanism is unlikely to be by charge neutralisation, but due to adsorption and bridging action. However, river water treated with these extracts presents two common features; firstly, the optimum coagulant dose that achieved the minimum residual turbidity was 40 mg/l, and secondly, at 20 mg/l dose, the zeta potential in the treated water remained unaltered at −12.4 mV from −12.3 mV across all the samples. This is clearly due to the background impact of zeta potential from other river water constituents (NOMs) in the system.

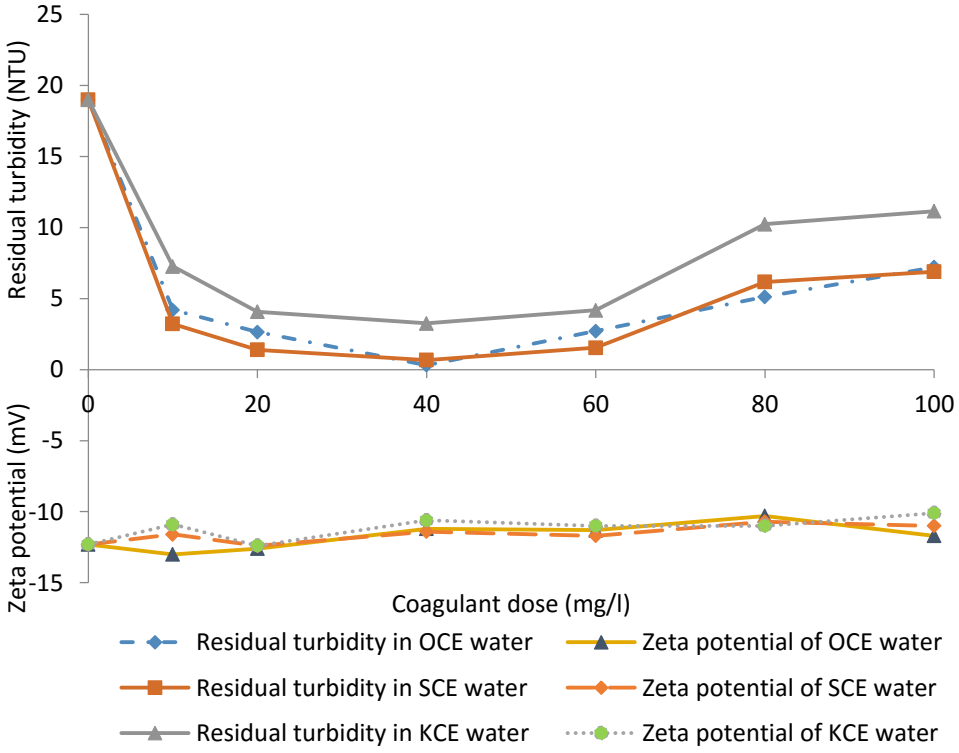

Figure 2: Coagulation mechanism of OCE, SCE and KCE in 19 NTU river water.

In addition, re-stabilisation was also observed after the addition of more coagulant dose in the water and the zeta potential increased accordingly. For instance, at 80 mg/l dose, the zeta potential of the final water was between −10.3 mV and −11.0 mV for all the extracts. At 100 mg/l dose, the final zeta potential value was reduced from −10.3 mV to −11.7 mV in OCE treated water.

The water sample which had been treated with 100 mg/l of SCE had an overall zeta potential reduction from −10.7 mV to −11.0 mV while that of KCE increases from −11.0 mV to −10.1 mV.

Again, measurement of the zeta potential of the treated water with 60 and 80 mg/l doses reveals a zeta potential of −11.0 mV with KCE as a coagulant. There was no consistency in the coagulation mechanism by the extracts in river water treatment. While the coagulation mechanism by the extracts was not consistent in river water, the overall removal of turbidity was considerably higher in river water than in the synthetic water. However, there were situations where the zeta potential of the treated water increased, but such an increase was not substantial enough to adjudge the coagulation mechanism to be due charge neutralisation action.

4. Discussion

Measurements of zeta potential before and after treatment in kaolin water using the three extracts show a significant increase in zeta potential in the treated water. Even though the coagulants are anionic, and kaolin particles are negatively charged as demonstrated by Katayon et al. (2004), the coagulation mechanism requires further investigation, because it unlikely by charge neutralisation. Most notably, during adsorption, kaolin particle can formed hydroxylated surfaces in water (Sharp, 2005). For optimum flocculation performance, zeta potential should be near zero (Kleimann *et al.*, 2005, Bolto and Gregory, 2007, Morfesis *et al.*, 2009). In all these cases, the zeta potential operating window of the extracts was $-6.67 < \zeta < -4.39$ mV, with minimal turbidity in the treated water. The difference in the zeta potential operating window was due to the coagulation mechanism by the natural extract, which was by adsorption and bridging While in the UK river water with multi-charged ions, metal coagulants are used, the effect of surface charge on the particles may be quite different.

The zeta potential of the river water presented in this work is within the range reported by (Sharp, 2005). The coagulation mechanism in river water was different due to background effect of NOM in the raw water. A similar observation was reported by Mpofu *et al.* (2003) who investigated anionic polyacrylamide acrylate copolymer in kaolin water. These findings suggest that the mechanism exhibited by Hibiscus extracts is unlikely to be via charge neutralisation, but rather by adsorption due to the positioning of the surface shear plane. River water may consist of variably charged ions and various NOM from different sources which may affect the coagulation mechanism. Many studies have shown that the presence of bivalent ions such as magnesium and calcium can also enhance flocculation activity (Tripathi *et al.*, 1976, Choy *et al.*, 2015). It is noteworthy that turbidity removal was higher in river water than synthetic water due to background effect of raw water constituents such as bivalent ions of calcium and magnesium.

5. Conclusion and recommendation

Zeta potential measurement played an important role to achieve the desired goal of water treatment. In this study, although all the samples are anionic, yet their mode of action were majorly by charge neutralisation, adsorption and bridging. The impact of the extract base on surface charge potential was clearly seen in treating both synthetic and river water. River water constituent impacted positively in the overall treatment process where turbidity removal was found to be significantly higher than that of synthetic water.

However, optimising the coagulation stage/unit by adopting zeta potential measurement would provide a more robust performance in water treatment.

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